Distribution and Cycling of Dissolved Organic Carbon and Colored Dissolved Organic Carbon on the West Florida Shelf

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LONG-TERM GOALS

The long-term goal of this project is to determine sources, sinks and dynamics of Colored Dissolved Organic Matter (CDOM) optical properties on spatial and temporal scales relevant to physical/biogeochemical/optical modeling efforts currently in progress for the West Florida Shelf HYCODE site. Predictive capability is needed for modeling in-water light attenuation and visibility in coastal regions. CDOM is one of the most significant and least understood light attenuating components, hence improved understanding of its optical properties, dynamics and spatial and temporal variability will result in improved radiance models in the littoral zone.

OBJECTIVES

The short-term goals are to characterize spatial and temporal variability in optical properties by determining sources and sinks of CDOM and Dissolved Organic Carbon (DOC) for the West Florida Shelf. The loss of CDOM by dilution/physical mixing and photobleaching will also be investigated. Photodegradation rates and effects of sunlight on CDOM optical properties and CDOC/DOC relationship as a function of CDOM source will be determined. This information will be applied to bio-optical and predictive light field models.

APPROACH

We propose to characterize spatial and temporal variability in optical properties and relative importance of the various sources and sinks of CDOM and Dissolved organic carbon (DOC) in the ECOHAB (Ecology of Harmful Algal Blooms)/HYCODE study area on the West Florida Shelf (between 27.5° - 26.0°N, 82.25° - 84.5° W, or roughly between Tampa Bay in the north to Charlotte Harbor in the south and 120 miles offshore). Sources to be studied include phytoplankton (diatoms, dinoflagellates, *Trichodesmium* spp.), rivers (Hillsborough, Manatee, Little Manatee, Alafia, Caloosahatchee and Peace Rivers), and sediments. We will also investigate loss of CDOM by dilution/physical mixing and photobleaching. Photodegradation rates and effects of sunlight on CDOM optical properties and CDOC/DOC relationship as a function of CDOM source will be determined. Analyses will include:

- Detailed surface mapping of CDOM and chlorophyll absorption, fluorescence and DOC concentration using AC-9 and SAFIre.

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14. ABSTRACT
The long-term goal of this project is to determine sources, sinks and dynamics of Colored Dissolved Organic Matter (CDOM) optical properties on spatial and temporal scales relevant to physical/biogeochemical/optical modeling efforts currently in progress for the West Florida Shelf HYCODE site. Predictive capability is needed for modeling in-water light attenuation and visibility in coastal regions. CDOM is one of the most significant and least understood light attenuating components, hence improved understanding of its optical properties, dynamics and spatial and temporal variability will result in improved radiance models in the littoral zone.

15. SUBJECT TERMS

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• Laboratory incubations of water samples using a solar simulator with subsequent measurement of DOC concentrations and CDOM fluorescence and absorption.

WORK COMPLETED

Since the beginning of this project in 1998, we have collected more than 1,000 samples between the Mississippi River and the Florida Keys. Sample analysis is nearly complete, and we are in the final phases of data analysis and publication. We submitted four papers for publication this past year, revisions have been completed, and we anticipate that all four will be published in 2004.

RESULTS

Data analysis has been completed for samples collected in the region of the Mississippi River plume, and we have found significant differences between seasons and between freshwater sources (Conmy et al., 2003). Concentrations of CDOM as measured by fluorescence at Ex = 300 nm, Em = 420 nm are shown in Figure 1. The mixing line was the same for the Mississippi River for 2000 and 2001, with a slope of -1.0. In contrast, the Atchafalaya River water contained higher concentrations in 2001, showing a 3-fold increase in the river endmember concentration and a slope for the mixing line of -6.0.

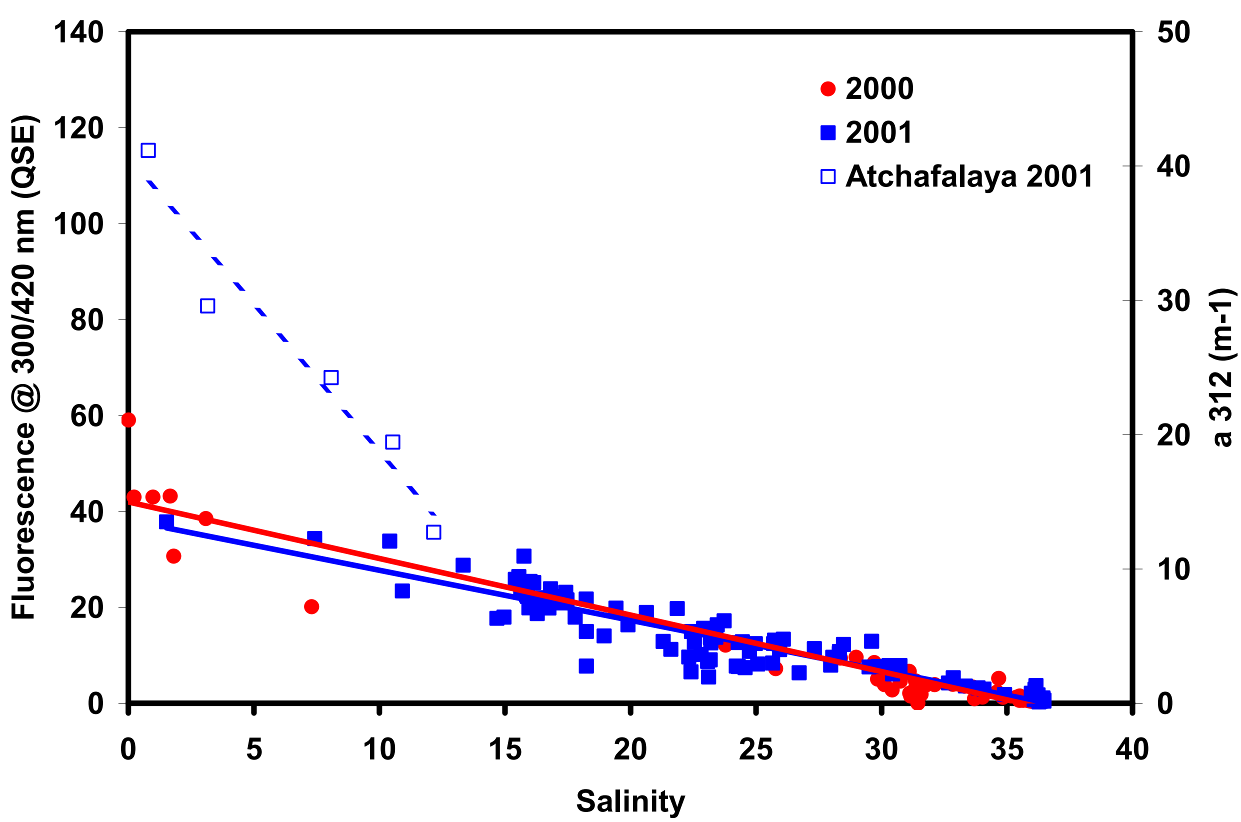

*Figure 1. CDOM fluorescence in relation to salinity for data collected in the Mississippi River outflow area. The zero salinity endmember is near 40 ppb QSE for the Mississippi River in both 2000 and 2001 and for the Atchafalaya River in 2000. However, in 2001, CDOM fluorescence in the Atchafalaya increased to 120 ppb QSE. Mixing relationships were linear for both years and both rivers, indicating that physical mixing is the dominant process controlling CDOM dist*ributions.

The spectral properties of the CDOM were also variable, with similarities between river endmembers when concentrations were similar, but distinct differences in the Atchafalaya River concurrently with elevated CDOM concentrations. All river endmember samples were distinctly different from marine samples collected offshore at seawater salinities (Conmy et al., 2003). Figure 2 shows normalized emission and excitation spectra for selected endmember samples. Normalization of spectra removes concentration differences and emphasizes spectral differences between samples. The top panel shows emission scans at excitation 300 nm normalized to the value at 450 nm. Marine samples have relatively flat emission spectra, indicative of photo-degraded CDOM.

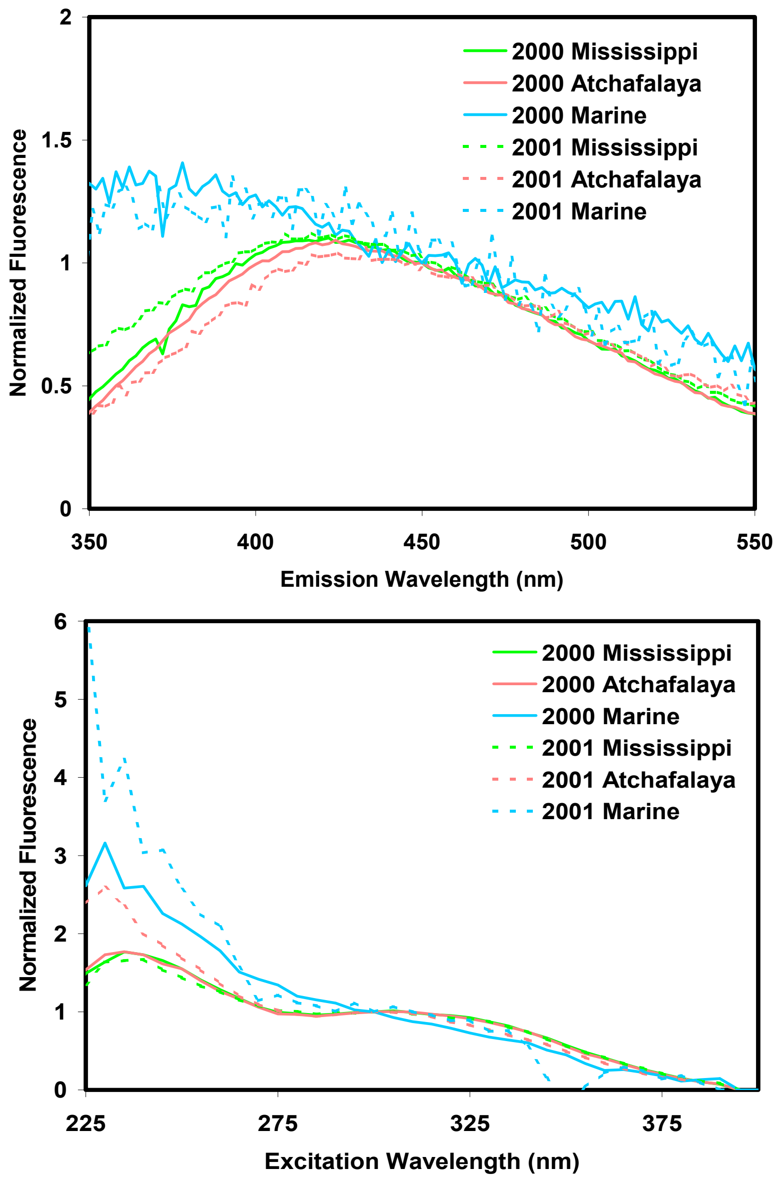

Figure 2. Normalized emission (top) and excitation (bottom) spectra for endmember samples from the Atchafalaya, Mississippi and marine regions in the northern Gulf of Mexico during 2000 and 2001 show differences due to CDOM composition variability. Flat spectra of marine samples and high ratios of UV-C:UV-B excited fluorescence are likely due to the effects of photo-degradation.

The bottom panel shows excitation spectra at emission 400 nm normalized to the value at 300 nm. Spectra differ primarily with respect to the relative fluorescence of the two humic peaks: A (peak around 240 nm) and C (peak around 320 nm). The Mississippi River has the lowest A:C ratio and C maximum is shifted towards longer wavelengths (red-shifted). This is common for riverine samples due to the presence of fresh humic material (Del Castillo et al., 2000; Coble, 1996). The marine samples have the highest A:C ratio and no distinct C peak maximum, most likely due to photo-degradation. The Atchafalaya is similar to the Mississippi in 2000, but intermediate between marine and riverine in 2001. Variations in the A:C ratio have been observed in estuaries (Prahl and Coble 1994) but underlying chemical causes are not well understood. It is generally thought that components which are excited at shorter wavelengths have lower molecular weight and fewer aromatic rings in their structure, but detailed chemical analyses were not performed as part of this study.

The combined results from the CDOM-salinity linear regression and spectral fluorescence characterizations resulted in improved identification of water mass source in this region, and enabled us to discriminate between Atchafalaya and Mississippi River CDOM. Demonstration that the concentration of CDOM in the Atchafalaya can, in some years, exceed that of the Mississippi by a factor of three will result in improved development of accurate algorithms, that take into consideration seasonal variability in discharge and composition of freshwater in this region.

IMPACT/APPLICATIONS

CDOM is one of the most significant and least understood light attenuating components in the ocean, hence improved understanding of its optical properties, dynamics and spatial and temporal variability will result in improved radiance models in the littoral zone. A major objective of this study is provide data for development and validation of coupled physical/ecological/bio-optical models which will incorporate phytoplankton, CDOM, suspended sediment distributions into models to account for hyperspectral water-leaving radiance $L_w(\lambda)$ and inherent optical properties (IOPs) fields.

RELATED PROJECTS

Our data will be integrated with data from several collaborative programs including: 1) an array of sixteen current meter (ADCP and ADV) moorings with meteorological instrumentation supported by multi-agency funding from State of Florida COMPS (Coastal Ocean Monitoring and PORTS Prediction System), NOAA/EPA-ECOHAB:Florida, and ONR-AUV programs, 2) bio-optical sensor packages on some of these moorings for continuous measurement of incoming irradiance, water-leaving radiance, hyperspectral downwelling irradiance, backscatter, forward scatter, absorption, attenuation and fluorescence funded by HYCODE/ONR (Carder/Steward, USF), 3) an ongoing program for monthly collection of CTD, phytoplankton dominant species cell counts, chlorophyll, phaeopigments, tow counts of macrozooplankton species and nutrient data (ECOHAB: Vargo et al., USF), 4) physical circulation model of WFS currents (Bob Weisberg and Mark Luther, USF), 6) coupled physical/ecological/bio-optical models which will incorporate phytoplankton, CDOM, suspended sediment distributions models for to account for hyperspectral water-leaving radiance $L_w(\lambda)$ and inherent optical properties (IOPs) fields (HYCODE – Walsh/Weisberg/Bissett) and 6) on-going SeaWiFS and MODIS ocean color studies on the West Florida Shelf (Frank Muller-Karger, USF).

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